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(71)Applicant : KONICA CORP

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(72)Inventor : HIRAI YOKO

NAKAI HIDEYUKI

SUZUKI TOSHITSUGU

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## (54) TREATMENT OF PHOTOSENSITIVE PLANOGRAPHIC PRINTING PLATE

### (57)Abstract:

PROBLEM TO BE SOLVED: To prevent a decrease in the processing rate or production of mold caused by circulation of a cleaning water used for the cleaning process before development by using a detergent containing at least one kind of chelating agent, surfactant and antiseptic.

SOLUTION: The cleaning liquid used in the cleaning process before development contains at least one kind selected from a chelating agent, surfactant and antiseptic. As for the solvent, water (such as city water) can be used. As for the chelating agent, a compd. which can form a chelate compd. by coordinate bonds with a metal ion can be used. The amt. of the chelating agent to be added preferably ranges from 0.0001 to 3.0wt.%. As for the surfactant, any of anion, nonion, cation or amphoteric surfactant can be used, and an anion or nonion surfactant is preferable. As for the antiseptic, phenol or its deriv., formalin, etc., can be used. The cleaning temp. is preferably controlled to 20 to 60°C.

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CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE  
INVENTION TECHNICAL PROBLEM MEANS EXAMPLE DESCRIPTION OF DRAWINGS  
DRAWINGS

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CLAIMS

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[Claim(s)]

[Claim 1] The art of the photosensitive lithography version characterized by being the penetrant remover in which the wash water used at this washing process contains a chelating agent in the art developed after wash water washes the photosensitive lithography version which prepared the water-soluble overcoat layer on the sensitization layer at a washing process.

[Claim 2] The art of the photosensitive lithography version characterized by being the penetrant remover in which the wash water used at this washing process contains a surfactant in the art developed after wash water washes the photosensitive lithography version which prepared the water-soluble overcoat layer on the sensitization layer at a washing process.

[Claim 3] The art of the photosensitive lithography version characterized by being the penetrant remover in which the wash water used at this washing process contains antiseptics in the art developed after wash water washes the photosensitive lithography version which prepared the water-soluble overcoat layer on the sensitization layer at a washing process.

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to speeding up and the stabilization technique of processing in an art including the processing which washes the photosensitive lithography version with wash water, and removes this overcoat layer before development, after image exposing the photosensitive lithography version which has a water-soluble overcoat on a sensitization layer.

[0002]

[Description of the Prior Art] In order to protect the film surface of the sensitization layer of the photosensitive lithography version which prepared the sensitization layer on the base material from a blemish or dust or to prevent oxidation reaction of a sensitization layer, a water-soluble overcoat layer may be prepared. When negatives are developed without removing an overcoat with pretreatment before development after image exposure, such a photosensitive lithography version is set in development, and it produces dispersion in the time amount from which an overcoat layer is dissolved and removed, and development unevenness is produced or it has a problem leading to the variation in sensibility.

[0003] In order to solve this problem, the method of rinsing the photosensitive lithography version and removing an overcoat layer before development, is learned. Since the amount of waste fluid will increase if it carries out by the approach (new liquid or \*\*\*\*\*) of throwing away using the wash water used for washing before development when an auto-processor performs this approach, the tank of wash water is usually formed and circulation reuse of wash water is performed. Although a supplement of wash water is performed in order to maintain the purpose with which carrying out of wash water and reduction of the wash water by evaporation are compensated, and the stability of processing when performing long-term running by such approach, the calcium ion then contained in water is also supplied to coincidence. This calcium ion became a cause, and the calcium carbonate carried out deposition and had become the inside of a tub, and piping with the decline in maintenance effectiveness, and the cause of failure.

[0004] Moreover, when long-term running was performed carrying out circulation reuse of the wash water used for washing before development by little liquid supplement, the resin concentration in wash water rose, the rate of washing processing fell, and it had become the cause of processing nonuniformity generating. Moreover, when the tank was made to store the washing processing liquid before development which contains resin in long-term running for a long period of time, mold occurred in processing liquid, the blinding of the pipe line arose and there was a problem which processing impossible produces in the end of running.

[0005]

[Problem(s) to be Solved by the Invention] Even if the technical problem which this invention tends to solve the problem of the above-mentioned Prior art, and this invention tends to solve carries out circulation reuse of the wash water used for washing before development, it is molding for the inside of a tub, or piping with the fall of the processing speed by the deposition of a calcium carbonate, or the rise of resin concentration, solving problems, such as generating, for them, and providing them with the art

of the photosensitive lithography version in which speeding up and stabilization of processing are possible.

[0006]

[Means for Solving the Problem] The means of this invention which solves the above-mentioned technical problem is following the (1) - (3).

[0007] (1) The art of the photosensitive lithography version characterized by being the penetrant remover in which the wash water used at this washing process contains a chelating agent in the art developed after wash water washes the photosensitive lithography version which prepared the water-soluble overcoat layer on the sensitization layer at a washing process.

[0008] (2) The art of the photosensitive lithography version characterized by being the penetrant remover in which the wash water used at this washing process contains a surfactant in the art developed after wash water washes the photosensitive lithography version which prepared the water-soluble overcoat layer on the sensitization layer at a washing process.

[0009] (3) The art of the photosensitive lithography version characterized by being the penetrant remover in which the wash water used at this washing process contains antiseptics in the art developed after wash water washes the photosensitive lithography version which prepared the water-soluble overcoat layer on the sensitization layer at a washing process.

[0010] Hereafter, this invention is explained in full detail.

[0011] It has a sensitization layer and an overcoat layer at least on a base material at this order, bloating tendency and solubility change with activity light, and the photosensitive lithography version processed by the art of this invention can form an image by processing with this developer. [ as opposed to a developer in this sensitization layer ]

[0012] The base material of the photosensitive lithography version processed by the art of this invention The well-known thing used as a base material of the photosensitive lithography version is included. For example, the metal plate which consists of aluminum, steel, zinc, copper, etc.; Plastic film, Paper in which the metal plate; plastic film with which chromium, zinc, copper, nickel, aluminum, iron, etc. were plated or vapor-deposited, glass plate; resin, etc. were applied; the plastic film with which metals, such as aluminum, were stuck and which carried out paper; hydrophilization processing is mentioned.

[0013] As a sensitization layer of the photosensitive lithography version processed by the art of this invention The sensitization layer containing diazo resin which is indicated by British patent No. 1,350,521, 1,460,978, and 1,505,739 each specification, The sensitization layer which consists of mixture of o-quinone diazide compound and novolak mold phenol resin which are indicated by JP,50-125806,A, The sensitization layer of an optical cross-linking photopolymer as concretely shown in the U.S. Pat. No. 3,860,426 specification, U.S. Pat. No. 4,072,527 -- said -- the 4th and the sensitization layer of the photopolymerization genotype photopolymer constituent indicated by No. 072528 each specification -- The sensitization layer which consists of mixture of the British patent No. 1,235,281, and an azide and a water-soluble polymer which is indicated by No. 1,495,861 each of this specification is mentioned.

[0014] The photosensitive lithography version which has a sensitization layer containing the following binder, a monomer, and a photopolymerization initiator as a desirable photosensitive lithography version processed by the art of this invention is mentioned.

[0015] As a binder, macromolecule polymers, such as a polyamide, polyester, a polycarbonate, polystyrene, polyurethane, polyvinyl chloride and its copolymer, polyvinyl resin, and acrylic resin, are mentioned, for example.

[0016] A macromolecule polymer desirable in these is a copolymerization macromolecule polymer obtained by following the (1) - (17) by copolymerizing the mixture of the monomer of a publication.

[0017] Into the above-mentioned monomer mixture, the above-mentioned monomer and other monomers which may be copolymerized may be mixed. Moreover, a giant-molecule polymer may embellish the copolymer obtained with the copolymer of the above-mentioned monomer by glycidyl acrylate, glycidyl methacrylate, etc.

[0018] (1) The monomer which has an aromatic series hydroxyl group, for example, o-hydroxystyrene,

p-hydroxystyrene, m-hydroxystyrene, o-hydroxyphenyl acrylate, p-hydroxyphenyl acrylate, m-hydroxyphenyl acrylate, etc.

[0019] (2) The monomer which has an aliphatic series hydroxyl group, for example, 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, N-methylol acrylamide, N-methylol methacrylamide, 4-hydroxy butyl methacrylate, 5-hydroxy pentyl acrylate, 5-hydroxy pentyl methacrylate, 6-hydroxy hexyl acrylate, 6-hydroxy hexyl methacrylate, N-(2-hydroxyethyl) acrylamide, N-(2-hydroxyethyl) methacrylamide, hydroxyethyl vinyl ether, etc.

[0020] (3) The monomer which has an amino sulfonyl group, for example, m-aminosulfonylphenylmethacrylate, p-aminosulfonylphenylmethacrylate, m-aminosulfonylphenylacrylate, p-aminophenyl acrylate, N-(p-amino sulfonyl phenyl) methacrylamide, N-(p-amino sulfonyl phenyl) acrylamide, etc.

[0021] (4) The monomer which has a sulfonamide radical, for example, N-(p-tosyl) acrylamide, N-(p-tosyl) methacrylamide, etc.

[0022] (5) alpha, beta-unsaturated carboxylic acid, for example, an acrylic acid, a methacrylic acid, a maleic acid, a maleic anhydride, itaconic-acid water, itaconic acid anhydride, etc.

[0023] (6) Alkyl acrylate which is not permuted [ a permutation or ], for example, methyl acrylate, ethyl-acrylate, acrylic-acid propyl, butyl acrylate, acrylic-acid amyl, acrylic-acid hexyl, acrylic-acid heptyl, acrylic-acid octyl, acrylic-acid nonyl, acrylic-acid DESHIRU, acrylic-acid undecyl, acrylic-acid dodecyl, acrylic-acid benzyl, acrylic-acid cyclohexyl, acrylic-acid-2-chloro ethyl, N, and N-dimethylamino ethyl acrylate, glycidyl acrylate, etc.

[0024] (7) Alkyl methacrylate which is not permuted [ a permutation or ], for example, methyl methacrylate, ethyl methacrylate, methacrylic-acid propyl, methacrylic-acid butyl, methacrylic-acid amyl, methacrylic-acid hexyl, methacrylic-acid heptyl, methacrylic-acid octyl, methacrylic-acid nonyl, methacrylic-acid DESHIRU, methacrylic-acid undecyl, methacrylic-acid dodecyl, methacrylic-acid benzyl, cyclohexyl methacrylate, methacrylic-acid-2-chloro ethyl, N, and N-dimethylaminoethyl methacrylate, glycidyl methacrylate, etc.

[0025] (8) Acrylamide or methacrylamide, for example, acrylamide, Methacrylamide, N-ethyl acrylamide, N-hexyl acrylamide, N-cyclohexyl acrylamide, N-phenyl acrylamide, N-nitrophenyl acrylamide, N-ethyl-N-phenyl acrylamide, N-(4-hydroxyphenyl) acrylamide, N-(4-hydroxyphenyl) acrylamide, (9) The monomer containing alkyl group fluoride, for example, trifluoro ethyl acrylate, Trifluoroethylmethacrylate, tetrafluoro propyl methacrylate, Hexafluoro propyl methacrylate, octafluoropentyl acrylate, octafluoropentyl methacrylate, heptadeca fluoro DESHIRU methacrylate, an N-butyl-N-(2-acryloxyethyl) heptadeca fluoro octyl sulfonamide, etc.

[0026] (10) Vinyl ether, for example, ethyl vinyl ether, 2-chloro ethyl vinyl ether, propyl vinyl ether, butyl vinyl ether, octyl vinyl ether, and phenyl vinyl ether

[0027] (11) Vinyl ester, for example, vinyl acetate, vinyl chloro acetate, vinyl butyrate, benzoic-acid vinyl, etc.

[0028] (12) Styrene, for example, styrene, methyl styrene, chloro methyl styrene, etc.

[0029] (13) Vinyl ketones, for example, a methyl vinyl ketone, an ethyl vinyl ketone, a propyl vinyl ketone, a phenyl vinyl ketone, etc.

[0030] (14) Olefins, for example, ethylene, a propylene, an isobutylene, a butadiene, an isoprene, etc.

[0031] (15) N-vinyl pyrrolidone, N-vinylcarbazole, 4-vinylpyridine, etc.

[0032] (16) The monomer which has a cyano group, for example, acrylonitrile, a methacrylonitrile, 2-pentene nitril, 2-methyl-3-butene nitril, 2-cyano ethyl acrylate, o-cyano styrene, m-cyano styrene, p-cyano styrene, etc.

[0033] (17) Monomer which has amino group, for example, N, and N-dimethylaminoethyl methacrylate, N, and N-dimethylamino ethyl acrylate, N, and N-dimethylaminoethyl methacrylate, polybutadiene urethane acrylate, N,N-dimethylaminopropyl acrylamide, N,N-dimethylacrylamide, acryloyl morpholine, N-isopropyl acrylamide, N, and N-diethyl acrylamide etc.

[0034] Although the above and a copolymer have that desirable whose polymerization average molecular weight measured by gel permeation chromatography (GPC) is 10,000-200,000, weight

average molecular weight is not limited to this range.

[0035] In this invention, especially an acrylic polymer is desirable among the above-mentioned high molecular compounds.

[0036] In the above-mentioned giant-molecule polymer, polyvinyl butyral resin, polyurethane resin, polyamide resin, polyester resin, an epoxy resin, novolak resin, natural resin, etc. may use together the giant-molecule polymer of other arbitration if needed. The content of these macromolecule polymers in a photosensitive constituent has 20 - 90% of the weight of the desirable range, and 30 - 70% of the weight of its range is still more desirable.

[0037] Well-known polymerization nature monomers can be used as a monomer. As a concrete compound, for example 2-ethylhexyl acrylate, Monofunctional acrylic ester and its derivative, or these acrylate, such as 2-hydroxyethyl acrylate and 2-hydroxypropyl acrylate, methacrylate, The compound replaced with itaconate, crotonate, maleate, etc., polyethylene-glycol diacrylate, Pentaerythritol diacrylate, bisphenol A diacrylate, 2 organic-functions acrylic ester and its derivative, or these acrylate of epsilon-caprolactone addition product of hydroxy pivalate neopentyl glycol, such as diacrylate, methacrylate, The compound replaced with itaconate, crotonate, maleate, etc., or trimethylolpropane triacrylate, The thoria chestnut rate of the isocyanuric acid by which EO denaturation was carried out, a pentaerythritol thoria chestnut rate, Pentaerythritol tetraacrylate, dipentaerythritol pentaacrylate, The compound which replaced polyfunctional acrylic ester and its derivative, or these acrylate, such as dipentaerythritol hexaacrylate and a pyrogallol thoria chestnut rate, with methacrylate, itaconate, crotonate, maleate, etc. can be mentioned.

[0038] Moreover, an acrylic acid or methacrylic acid is introduced into the oligomer of suitable molecular weight, and what is called the so-called prepolymer which gave photopolymerization nature can be used suitably.

[0039] In addition, the compound of a publication etc. can be mentioned to JP,58-212994,A, 61-6649, 62-46688, 62-48589, 62-173295, 62-187092, 63-67189, JP,1-244891,A, etc., and the compound of a publication etc. can be further used for "chemistry goods of 11290" Chemical Daily, and p.286-294 suitably in this invention the compound of a publication, a "UV-EB hardening handbook (volume on raw material)" macromolecule publication meeting, and p-11-65.

[0040] In these, the compound which has two or more acrylic radicals or methacrylic radicals in intramolecular is desirable in this invention, and 5,000 or less thing has [ 10,000 or less ] more preferably more desirable still molecular weight. Moreover, in this invention, one sort or two sorts or more in these monomers or a prepolymer can be mixed and used.

[0041] as a photopolymerization initiator -- for example, J. Koser (J. Kosar) work "light sensitive systems" -- a diazo compound, a halogenated compound, photoreduction nature coloring matter, etc. are mentioned to a carbonyl compound which is indicated by Chapter 5, an organosulfur compound, persulfide, a redox system compound, and an azo list. Furthermore, the concrete compound is indicated by the British patent No. 1,459,563.

[0042] That is, the following can be used as a photopolymerization initiator. For example, benzoin methyl ether, benzoin iso-propyl ether, Benzoin derivatives, such as an alpha and alpha-dimethoxy-alpha-phenyl acetophenone; A benzophenone, 2, a 4-dichloro benzophenone, methyl o-benzoylbenzoate, Benzophenone derivative;2-KURORU thioxan tons, such as a 4 and 4'-screw (dimethylamino) benzophenone, Thioxan ton derivatives, such as 2-isopropyl thioxan ton; 2-KURORU anthraquinone, Anthraquinone derivatives, such as 2-methyl anthraquinone; N-methyl acridone, acridone derivative;alpha [, such as N-butyl acridone, ] and alpha-diethoxy acetophenone; benzyl full -- me -- non, everything but a; xanthone; uranyl compound JP,59-1281,B JP,61-9621,B and a triazine derivative given in JP,60-60104,A, JP,59-1504,A and organic peroxide given in JP,61-243807,A, JP,43-23684,B, JP,44-6413,B, JP,44-6413,B, JP,47-1604,B and a diazonium compound given in U.S. Pat. No. 3,567,453, U.S. Pat. No. 2,848,328, U.S. Pat. No. 2,852,379, and an organic azide compound given in U.S. Pat. No. 2,940,853, JP,36-22062,B, JP,37-13109,B, JP,38-18015,B, and orthoquinone diazido given in JP,45-9610,B JP,55-39162,B, JP,59-14023,A, and "macro leakage-at-bulb KYURUSU (Macromolecules), The 10th volume, various onium compounds given in the 1307th page (1977), An azo

compound given in JP,59-142205,A, JP,1-54440,A, The European Patent No. 109,851, the European Patent No. 126,712, "Journal OBU imaging Science" (J. Imag.Sci.)", The 30th volume, a metal allene complex given in the 174th page (1986), Japanese Patent Application No. No. 56831 [ four to ], and a sulfonium (oxo-) organic boron complex given in Japanese Patent Application No. No. 89535 [ four to ], Titanocene given in JP,61-151197,A, "a coordination chemistry review (Coordinantion Chemistry Review)", the 84th volume and the 85- the transition metal complex containing transition metals, such as a ruthenium the 277th page (1988) and given in JP,2-182701,A, -- The publications 2 and 4 of JP,3-209477,A, 5-thoria reel imidazole dimer, carbon tetrabromide, an organic halogenated compound given in JP,59-107344,A, etc. are mentioned.

[0043] As an overcoat layer of the photosensitive lithography version processed by the art of this invention In using only for the purpose which protects a sensitization stratification plane What is dissolved in the wash water which has film-forming and is used at the washing process before development, It has the sensitization layer of radical polymerization nature, and the overcoat layer using the polymer which expected the polymerization prohibition operation by the oxygen in air, and was excellent in oxygen cutoff nature, such as polyvinyl alcohol and acid celluloses, etc. is mentioned. Moreover, a thing like a JP,55-49729,B publication is also contained, for example. Furthermore, in order that the overcoat layer of the photosensitive lithography version concerning this invention may improve the shape of a field, the surfactant may be added again.

[0044] When the photosensitive lithography version of this invention is [ a sensitization layer ] a photopolymerization nature sensitization layer, as for an overcoat layer, it is desirable that the solubility to the developer (generally alkali water solution) mentioned later is high. If the desirable example of a compound is given, polyvinyl alcohol, the poly saccharide, a polyvinyl pyrrolidone, a polyethylene glycol, gelatin, glia, casein, hydroxyethyl cellulose, a carboxymethyl cellulose, methyl cellulose, hydroxyethyl starch, gum arabic, SAKUROZUOKUTA acetate, ammonium alginate, sodium alginate, a polyvinyl amine, polyethylene oxide, polystyrene sulfonate, polyacrylic acid, a water-soluble polyamide, etc. will be mentioned. Independent or the thing mixed two or more sorts can be used for these compounds as a principal component. As a desirable compound, polyvinyl alcohol is mentioned especially.

[0045] These compounds are dissolved in a suitable solvent, on a photopolymerization nature sensitization layer, spreading desiccation is carried out and an overcoat layer is formed.

[0046] 0.1-5.0 micrometers is desirable especially desirable, and the thickness of an overcoat layer is 0.5-3.0 micrometers.

[0047] An overcoat layer can contain a mat agent etc. if needed further.

[0048] In this invention, the penetrant remover used at the washing process before development is the liquid containing at least one sort chosen from a chelating agent, a surfactant, and antiseptics, and can use water (for example, tap water) as a solvent.

[0049] The compound which carries out coordinate bond to a metal ion, and forms a chelate compound as a chelating agent is used. Ethylene-diamine-tetraacetic acid, its potassium salt, its sodium salt, A triethylenetetramine hexa acetic acid, its potassium salt, its sodium salt, Diethylenetriaminepentaacetic acid, its potassium salt, its sodium salt, A hydroxyethyl ethylene JIAMINTORI acetic acid, its potassium salt, its sodium salt, A nit RIOTORI acetic acid, its potassium salt, its sodium salt, 1-hydroxy ethane -1, 1-diphosphonic acid, The potassium salt, its sodium salt, friend NOTORI (methylene phosphonic acid), its potassium salt, its sodium salt, phosphono alkane tricarboxylic acid, etc. are mentioned. As for these chelating agents, what has an organic amine salt instead of potassium salt and sodium salt is effective.

[0050] 0.0001 - 3.0% of the weight of the range is suitable for the addition of a chelating agent.

[0051] As a surface active agent, although any surface active agent of an anion, Nonion, a cation, and both sexes can be used, an anion or a nonionic surface active agent is desirable. The class of desirable surface active agent changes with presentations of an overcoat layer or a sensitization layer, and generally serves as a dissolution accelerator of an overcoat layer material, and what has the small solubility of a sensitization layer component is desirable.

[0052] As an anionic surface active agent, fatty-acid salts, loon chain acid chloride, and hydroxy alkane sulfonates Alkane sulfonates, dialkyl sulfo succinate, and alkylbenzene sulfonates

Alkylnaphthalenesulfonate and alkyl phenoxy polyoxyethylene PUROPIRUSURUHON acid chloride Polyoxyethylene alkyl sulfophenyl ether salts and N-methyl-N-oleyl taurine sodium N-alkyl sulfo succinic-acid monoamide disodium salts and petroleum sulfonates Sulfation castor oil, a sulfation beef tallow oil, the sulfate salts of aliphatic alkylester, Alkyl-sulfuric-acid ester salts, polyoxyethylene-alkyl-ether sulfate salts, Fatty-acid monoglyceride sulfate salts, polyoxyethylene styryl phenyl ether sulfate salts, Alkyl phosphoric ester salts, polyoxyethylene-alkyl-ether phosphoric ester salts, Polyoxyethylene-alkyl-phenyl-ether phosphoric ester salts, the partial saponification objects of a styrene-maleic-anhydride copolymerization object, the partial saponification objects of an olefin-maleic-anhydride copolymerization object, and naphthalene sulfonate formalin condensates are mentioned.

[0053] As a nonionic surface active agent, polyoxyethylene alkyl ether Polyoxyethylene alkyl phenyl ether and polyoxyethylene poly styryl phenyl ether Polyoxyethylene PORIOKIEI propylene alkyl ether and glycerine fatty acid esters Sorbitan fatty-acid partial ester and pentaerythritol fatty-acid partial ester Propylene glycol mono-fatty acid ester and cane-sugar fatty-acid partial ester Polyoxyethylene sorbitan fatty-acid partial ester and IECHIREN glycol fatty acid ester PORII glycerol fatty-acid partial ester and polyoxyethylene-ized castor oil Polyoxyethylene glycerol fatty-acid partial ester, fatty-acid diethanolamide, N, and N-screw-hydroxy alkylamines, polyoxyethylene alkylamine, triethanolamine fatty acid ester, a trialkyl amine oxide, etc. are mentioned.

[0054] The desirable addition of a surfactant is 0.005 - 10 % of the weight. Moreover, a defoaming agent can also be used together to a surfactant.

[0055] As antiseptics, derivatives, such as a phenol or its derivative, formalin, an imidazole derivative, sodium dehydroacetate, a 4-iso thiazoline-3-ON derivative, benzo iso thiazoline-3-ON, a benzotriazol derivative, an amidine guanidine derivative, quaternary ammonium salt, PIROJIN, a quinoline, and guanidine, diamond gin, a triazole derivative, oxazole, an oxazine derivative, etc. are mentioned.

[0056] In the washing approach of this invention, as for the penetrant remover used for washing before development, it is desirable to adjust and use temperature, and this temperature has the desirable range of 20-60 degrees C. Well-known processing liquid supply techniques, such as a spray, a DIP, and spreading, can be used for the approach of washing, and processing promotion means, such as a brush and a shower in liquid in a diaphragm roll and DIP processing, can be suitably used for it.

[0057] In this invention, a development may be immediately performed after front [ development ] washing process termination, and after making it dry after the washing process before development, a development may be performed. After a development process can perform well-known after treatment, such as rinsing, a rinse, and gum length.

[0058] The developer in the art of this invention is a developer used for the development of said photosensitive lithography version. Diazo resin and a photopolymerization nature constituent are used as a photosensitive component. For example, the developer for negatives for the slack negative-mold photosensitivity lithography versions, The developer for positives for the positive type photosensitivity lithography versions using o-quinone diazide compound as a photosensitive component and the developer both for a negative positive both for the above-mentioned negative-mold photosensitivity lithography version and the positive type photosensitivity lithography version are mentioned. In the art of this invention, developers may be any of the well-known above-mentioned developer for negatives, the developer for positives, and the developer both for a negative positive.

[0059] In the art of this invention, although a developer changes also with photosensitive lithography versions to develop, it consists of alkali chemicals and other additives typically. In this developer, as for pH of a developer, eight or more are desirable, and 12 or more are especially desirable.

[0060] As alkali chemicals, although various kinds of things can be used, it is desirable to use silicic-acid alkali. As silicic-acid alkali which can be used, a potassium silicate, a sodium silicate, a meta-sodium silicate, a meta-potassium silicate, silicic-acid ammonium, etc. are mentioned, for example. As for these silicic-acids alkali, it is desirable to make it contain in 0.3 - 10% of the weight of the range in a developer. Moreover, as for SiO<sub>2</sub> concentration in silicic-acid alkali, it is desirable that it is in 0.1 -

7.0% of the weight of the range.

[0061] As alkali chemicals which can use alkali chemicals other than the above-mentioned silicic-acid alkali for a developer, and can be used for it For example, a potassium hydroxide, a sodium hydroxide, a lithium hydroxide, the third sodium phosphate, Sodium diphosphate, the third potassium phosphate, the second potassium phosphate, The third ammonium phosphate, dibasic calcium phosphate, a meta-sodium silicate, Organic alkali chemicals like inorganic alkali chemicals, such as sodium bicarbonate, a sodium carbonate, potassium carbonate, and an ammonium carbonate, monochrome, JI or triethanolamine, and hydroxylation tetra-alkyl can be mentioned. Also in these, a potassium hydroxide or a sodium hydroxide is desirable.

[0062] The organic solvent other than the above-mentioned alkali chemicals can be added. Ten or less % of the weight of a thing has the desirable solubility to the water which can be set 20 degrees C as an organic solvent. For example, ethyl acetate, propyl acetate, butyl acetate, benzyl acetate, ethylene glycol monobutyl ASETO, Carboxylate like butyl lactate and rep phosphoric-acid butyl; Ethyl butyl ketone, Methyl isobutyl ketone and the ketones like a cyclohexanone; Ethylene glycol monobutyl ether, Ethylene glycol benzyl ether, ethylene glycol monophenyl ether, Propylene glycol, phenyl propylene glycol, benzyl alcohol, Alkylation aromatic hydrocarbon like an alcohols; xylene like methylphenylcarbinol, n-amyl alcohol, and methyl amyl alcohol; Methylene dichloride, Halogenated hydrocarbon; like ethylene dichloride and mono-chlorobenzene can be mentioned. These organic solvents are independent respectively, or can be used combining two or more sorts.

[0063] In a developer, other various well-known additives can be added with each purpose in addition to the above-mentioned alkali chemicals and an organic solvent. As these additives, a reducing agent, a high contrast-ized agent, a chelating agent, a surface active agent, and an organic carboxylic acid are mentioned.

[0064] There is an inorganic and organic reducing agent as a reducing agent. As an inorganic reducing agent, although phosphate, such as sulfites, such as a sodium sulfite, potassium sulfite, ammonium sulfite, a sodium hydrogensulfite, and a potassium hydrogensulfite, a sodium phosphite, potassium hypophosphite, sodium hydrogenphosphite, a phosphorous acid hydrogen potassium, phosphorous acid 2 hydrogen sodium, and phosphorous acid hydrogen 2 potassium, a hydrazine, a sodium thiosulfate, a sodium dithionite, etc. can be mentioned, a reducing agent excellent in especially effectiveness is a sulfite, for example. As an organic reducing agent, amine compounds, such as phenolic compounds, such as the organic reducing agent of water solubility or alkali fusibility, for example, hydroquinone, Metol, a methoxy quinone, thiosalicylic acid, resorcinol, and 2-methyl resorcinol, a phenylenediamine, and phenylhydrazine, can be mentioned. As for these reducing agents, it is desirable to make it contain 0.1 to 10% of the weight in a developer, and it is more desirable to make it contain 0.5 to 5% of the weight.

[0065] Although what [ various kinds of ] is well-known as a high contrast-ized agent can be used, the compound which has a polyethylene oxide radical is desirable. The Nonion nature surface active agent which has a polyethylene oxide radical especially, and the Nonion nature surface active agent which has a polyethylene oxide radical and an alkyl group especially are desirable.

[0066] The Nonion nature surface active agent which has a polyethylene oxide radical has three or more ethyleneoxide radicals, and its nonionic surface active agent whose HLB an HLB (Hydrophile-Lipophile Balance) value is 8-20 further five or more is more desirable. Moreover, as a nonionic surface active agent, what has a propylene oxide radical with an ethyleneoxide radical is desirable. That whose HLB value is eight or more especially is more desirable.

[0067] As a desirable example of the compound which has a polyethylene oxide radical, the compound expressed with following general formula [1]- [8] is mentioned.

[0068]

[Formula 1]

h

g cg b

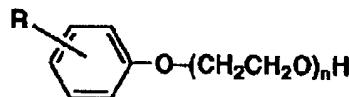
eb cg e e

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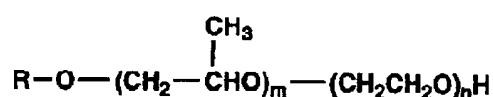
一般式 [1]



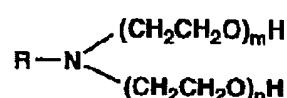
一般式 [2]



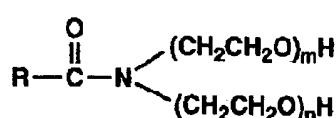
一般式 [3]



一般式 [4]



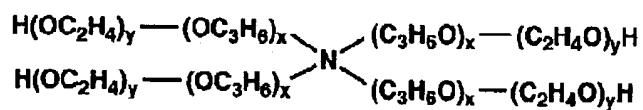
一般式 [5]



一般式 [6]



一般式 [7]



一般式 [8]



[0069] General formula [ In a 1]- [8] type, R expresses a hydrogen atom or a univalent organic radical, and a, b, c, m, nx, and y express the integer of 1-40 respectively.

[0070] A straight chain or the alkyl group of the carbon numbers 1-30 of branching, the alkyl group that has a substituent [for example, aryl groups (phenyl group etc.)], the alkyl carbonyl group whose alkyl part is the alkyl group of a straight chain or the carbon numbers 1-30 of branching, the phenyl group which may have substituents (for example, hydroxyl, the above alkyl groups, etc.) are mentioned by the organic radical expressed with R, and the bottom.

[0071] Next, the example of a high contrast-ized agent is shown.

[0072] A polyethylene glycol, the polyoxyethylene lauryl ether, the polyoxyethylene nonyl ether, The polyoxyethylene cetyl ether, polyoxyethylene stearylether, The polyoxyethylene oleyl ether,

polyoxyethylenebehenyl ether, The polyoxyethylene polyoxypropylene cetyl ether, polyoxyethylene polyoxypropylene behenyl ether, The polyoxyethylene nonylphenyl ether, polyoxyethylene octyl phenyl ether, A polyoxyethylene stearyl amine, a polyoxyethylene oleyl amine, Polyoxyethylene octadecanamide, polyoxyethylene oleic amide, Polyoxyethylene castor oil, polyoxyethylene loon ethyl ether, The polyoxyethylene lanolin ether, polyoxyethylene mono-laurate, Polyoxyethylene monostearate, polyoxyethylene glyceryl mono-olate, Polyoxyethylene glyceryl monostearate, polyoxyethylene propylene glycol monostearate, Oxyethylene oxypropylene block polymer, a JISUCHIREN-ized phenol polyethylene oxide addition product, A tribenzylphenol polyethylene oxide addition product, an octyl phenol polyoxyethylene polyoxypropylene addition product, glycerol monostearate, sorbitan monolaurate, polyoxyethylene sorbitan monolaurate, etc.

[0073] The weight average molecular weight of the compound which has a polyethylene oxide radical has the desirable range of 300-10000, and especially its range of 500-5000 is desirable.

[0074] Although what [ various kinds of ] is well-known as a chelating agent can be used For example, polyphosphoric acid and its sodium salt, potassium salt, and ammonium salt, Ethylene-diamine-tetraacetic acid, diethylenetriaminepentaacetic acid, a triethylenetetramine hexa acetic acid, Amino polycarboxylic acid and those sodium salt, such as a hydroxyethyl ethylene JIAMINTORI acetic-acid, nitrilotriacetic acid, 1, and 2-diamino cyclohexane tetra-acetic-acid and 1, and 3-diamino-2-propanol tetra-acetic acid, Potassium salt and ammonium salt, friend NOTORI (methylene phosphonic acid), An ethylenediamine tetrapod (methylene phosphonic acid), diethylenetriamine PENTA (methylene phosphonic acid), Triethylenetetramine hexa (methylene phosphonic acid), hydroxyethyl ethylene JIAMINTORI (methylene phosphonic acid) and 1-hydroxy ethane -1, 1-diphosphonic acid and those sodium salt, potassium salt, and ammonium salt can be mentioned.

[0075] Although the optimum value of the amount used changes with degrees of hardness, amounts, etc. of the class of chelating agent, and hard water used when using a chelating agent, it is usually more preferably used 0.01 to 5% of the weight to the developer at the time of use in 0.01. - 0.5% of the weight of the range. If there are few additions of a chelating agent, the desired end will not fully be attained, but if there are many additions, the bad influence to the image section will come out of a color omission etc.

[0076] As a surface active agent, a cationic surface active agent, an anionic surface active agent, an amphoteric surface active agent, etc. are mentioned.

[0077] These all can be used although a cationic surface active agent is divided roughly into an amine mold and a quaternary-ammonium-salt mold.

[0078] As an example of an amine mold, there are polyoxyethylene alkylamine, N-alkyl propylene amine, N-alkyl polyethylene polyamine, N-alkyl polyethylene polyamine dimethyl sulfate, an alkyl biguanide, a long-chain amine oxide, alkyl imidazoline, 1-hydroxyethyl-2-alkyl imidazoline, 1-acetyl aminoethyl-2-alkyl imidazoline, 2-alkyl-4-methyl-4-hydroxymethyl oxazoline, etc.

[0079] As an example of a quaternary-ammonium-salt mold, moreover, a long-chain primary amine salt, an alkyl trimethylammonium salt, A dialkyl dimethyl ethylammonium salt, alkyldimethyl ammonium salt, An alkyl dimethylbenzyl ammonium salt, alkyl pyridinium salt, An alkyl quinolinium salt, an alkyl iso quinolinium salt, an alkyl pyridinium sulfate, Steer RAMIDO methyl pyridinium salt, an acylamino ethyl diethylamine salt, An acylamino ethyl MECHIRUJI ethylammonium salt, an alkylamide propyl dimethylbenzyl ammonium salt, A fatty-acid polyethylene polyamide, acylamino ethyl pyridinium salt, ASHIRUKORAMINO formyl methyl pyridinium salt, SUTEARO oxymethyl pyridinium salt, Fatty-acid triethanolamine, fatty-acid triethanol AMINGI acid chloride, There are trioxyethylene fatty-acid triethanolamine, fatty-acid dibutylamino ethanol, cetyl oxymethyl pyridinium salt, a p-iso octyl phenoxy ethoxyethyl dimethylbenzyl ammonium salt, etc. (The "alkyl" in the example of the above-mentioned compound shows the straight chain or the alkyl permuted in part of carbon numbers 6-20, and, specifically, straight chain alkyls, such as hexyl, octyl, cetyl, and stearyl, are used preferably.) In these, the cationic surface active agent of a water-soluble quaternary-ammonium-salt mold is especially effective, and an alkyl trimethylammonium salt, an alkyl dimethylbenzyl ammonium salt, ethylene oxide addition ammonium salt, etc. are suitable also in it. Moreover, in large semantics, the polymer which repeats a cation component and it has as a unit is also a cationic surface active agent, and

is \*\*\*\*(ed) by the cationic surface active agent. Especially the polymer containing the quaternary ammonium salt obtained by copolymerizing with an oleophilic monomer can be used suitably. The range of the weight average molecular weight of this \*\*\*\*\* is 300-50000, and the range of it is 500-5000 especially preferably. These cationic surface active agents are used independently, and also they may use two or more sorts together.

[0080] as an anion mold surfactant -- higher-alcohol (C8-C22) sulfate salts -- [ -- for example The sodium salt of lauryl alcohol sulfate, the sodium salt of octyl alcohol sulfate, The ammonium salt of lauryl alcohol sulfate, TeePol-81 (product made from trade name shell chemistry), ] fatty alcohol phosphate, such as the second sodium alkyl sulfate (For example, the sodium salt of cetyl alcohol phosphoric ester, etc. and alkylaryl sulfonates) for example, the sodium salt of dodecylbenzenesulfonic acid and the sodium salt of an isopropyl naphthalene sulfonic acid -- The nari TOUMU salt of a JINAFU thalline disulfon acid, the sodium salt of a meta-nitrobenzene sulfonic acid, etc., There are sulfonates (for example, C17H33CON(CH<sub>3</sub>) CH<sub>2</sub>SO<sub>3</sub>Na etc.) of alkylamide and sulfonates (for example, sodium sulfo succinic-acid dioctyl ester, sodium sulfo succinic-acid dihexyl ester, etc.) of dibasicity fatty acid ester. Sulfonates are suitably used especially in these.

[0081] As an amphoteric surface active agent, a compound like N-methyl-N-pentadecyl aminoacetic acid sodium can be used, for example.

[0082] As for a surfactant, it is desirable to make a developer contain by the concentration of 0.1 - 10% of the weight of the range.

[0083] As an organic carboxylic acid, the aliphatic carboxylic acid and aromatic carboxylic acid of the carbon atomic numbers 6-20 can be mentioned. As a concrete example of aliphatic carboxylic acid, there are a caproic acid, enanthyllic acid, a caprylic acid, a lauric acid, a myristic acid, a palmitic acid, stearin acid, etc., and especially a desirable thing is the alkane acid of carbon numbers 8-12. Moreover, the thing of the chain with which the unsaturated fatty acid which has a double bond also branched in the chain may be used. Aromatic carboxylic acid is \*\*\*\*\* by which the carboxyl group was permuted by the \*\* NZEN ring, the naphthalene ring, the anthracene ring, etc. specifically O-chlorobenzoic acid, para chlorobenzoic acid, o-hydroxybenzoic acid, Para hydroxybenzoic acid, o-aminobenzoic acid, p-aminobenzoic acid, 2, 4-dihydroxybenzoic acid, 2, 5-dihydroxybenzoic acid, 2, 6-dihydroxybenzoic acid, 2, 3-dihydroxybenzoic acid, 3, 5-dihydroxybenzoic acid, a gallic acid, Although there are a 1-hydroxy-2-naphthoic acid, a 3-hydroxy-2-naphthoic acid, a 2-hydroxy-1-naphthoic acid, a 1-naphthoic acid, a 2-naphthoic acid, etc., especially the hydroxy naphthoic acid is effective. In order to raise water solubility, as for the above-mentioned aliphatic series and aromatic carboxylic acid, it is desirable to use as sodium salt, or potassium salt or ammonium salt. When using an organic carboxylic acid, there is no limit with the exceptional amount of the organic carboxylic acid used, but when lower than 0.1 % of the weight, the dissolution may be barred at when [ whose effectiveness is not enough / that an improvement of the effectiveness beyond it cannot be measured at 10 % of the weight or more, and when using another additive together ]. Therefore, a desirable addition is 0.1 - 10 % of the weight to the developer at the time of use, and is 0.5 - 4 % of the weight more preferably.

[0084] Although the component of the remainder of a developer is water, the various additives further known for this industry if needed, for example, a defoaming agent etc., can be made to contain.

[0085]

[Example] Although an example explains this invention still more concretely below, this invention is not limited to these.

[0086] The front face of the aluminum plate (the quality of the material 1050, temper H16) of 0.3mm thickness of production of an example 1 photosensitivity record ingredient was degreased in the sodium-hydroxide water solution 3%, electrolytic etching was carried out by 25 degrees C and 50 A/dm<sup>2</sup> in 2% hydrochloric-acid bath, the anodic oxide film of 3 g/m<sup>2</sup> was prepared in 30% sulfuric-acid bath after rinsing, the meta-sodium-silicate water solution performed 85 degrees C and hydrophilization processing during 10 seconds 2%, and the base material was produced.

[0087] The coating liquid for sensitization layers of the following presentation was applied using the wire bar on this base material, it dried for 2 minutes at 80 degrees C, and the sensitization layer of 2.0

micrometers of thickness after desiccation was prepared. The coating liquid for overcoat layers of the following presentation on this sensitization layer was applied so that it might become 2-micrometer thickness using an applicator, it dried for 3 minutes at 80 degrees C, the overcoat layer was prepared, and the photosensitive record ingredient was produced.

[0088]

Coating liquid for sensitization layers High molecular compound 6.0g

Dipentaerythritolmonohydroxypentaacrylate 4.0g 2, 4-screw -6 (TORIKURORO methyl) - (p-methoxy styryl)

- s-triazine 0.5g Polyacrylic acid (JURIMAAC10L, Nippon Junyaku make) 0.02g Fluorochemical surfactant (FC-430, Sumitomo 3 M company make) 0.01g Coloring matter (Victoria PYUA blue BOH, the Hodogaya chemistry company make) 0.02g Methyl lactate 180ml 2-ethoxy propanol Coating liquid for 20ml overcoat layers Polyvinyl alcohol (oxygen transmittance: 0.5 MW:35000)

97 weight sections Surface active agent (Bayer make FT-248) Three weight sections Water The following development mother liquor was taught to 1l. and a developer tank 2, 3l. of tap water was taught to 9l. and a rinse tank 3 for penetrant remover \*\* before the following development at the washing tub 1 before development of the auto-processor shown in 900 weight sections drawing 1, the auto-processor was set and the development of the above-mentioned photosensitive lithography version which carried out image exposure was performed. In the development, said photosensitive lithography version of 2 was processed 600m every 2 20m in 30 days on the 1st, filling up 50ml of front

[ development ] penetrant removers, 25ml of development replenishers which diluted the following concentration development replenisher 4 times, and 50ml of rinsing water, whenever it let the photosensitive lithography version pass 1m2. In addition, processing conditions made washing before development and made development 25-degree-C 20 seconds for 25-degree-C 3 seconds. When the effluent of the penetrant remover before development after this processing and in the front

[ development ] washing tub 1 was carried out and the penetrant remover before development was observed, fixing of a sludge component was not accepted but was able to be cleaned easily.

[0089] In drawing 1 A the development section and C for the front [ development ] washing section and B In addition, the rinsing section, T extracts the guide roll for the photosensitive lithography version conveyance, and 16 for the conveyance way of the photosensitive lithography version, and 11-15, a roll and 17 are [ a shower nozzle, and 19a and 19b of a development brush, and 18a and 18b ] pumps, and \*1, \*1, \*2, and \*2 are connected for piping among drawing, respectively.

[0090] When tap water was used as a front [ example of comparison 1 development ] penetrant remover and also the same experiment as an example 1 was conducted, hard solid content fixed to the washing tub before development after processing, it ground against washing with the brush, and washing was required.

[0091] Using penetrant remover \*\* before the following development as a front [ example 2 development ] penetrant remover, the amount of supplements was set to 5ml per two the 1m of the photosensitive lithography versions, and also the same experiment as an example 1 was conducted. Although the amount of supplements of the penetrant remover before development was 10% of the example 1, the detergency of an overcoat layer is good and was able to be processed satisfactory by quick 25-degree-C processing for 3 seconds through running.

[0092] Tap water was used as a front [ example of comparison 2 development ] penetrant remover, and also the same experiment as an example 2 was conducted. When the dissolution rate of an overcoat layer became slow and processing was continued for 25-degree-C 3 seconds from the neighborhood where throughput exceeded 2 100m, the photosensitive lithography version was carried to the development section in the condition that an overcoat layer is not removed completely.

[0093] When processing of the photosensitive lithography version was made into 1 120 days with an every [ 2 ] of 5m [ per day ] and also the same experiment as an example 1 was conducted, using penetrant remover \*\* before the following development as a front [ example 3 development ] penetrant remover, the development was able to be carried out to stability through running.

[0094] Tap water was used as a front [ example of comparison 3 development ] penetrant remover, and

also the same experiment as an example 3 was conducted. The liquid amount of supply from the shower nozzle of the washing section before development began to decrease from near the 70th day. When the pipe line was checked on the 80th, mold occurred in the wall and circulation of liquid was barred. [0095]

A developer Development mother liquor Concentration development replenisher Water The 590 weight sections 82 weight sections beta-ANIRINO ethanol The 0.3 weight section The 0.3 weight sections Propylene glycol The 0.3 weight section The 0.6 weight sections 2-hydroxy-3-naphthoic acid 0.6 weight section 0.6 weight sections p-tert-butyl benzoic acid The 1.2 weight sections The 1.5 weight sections Emulgen 147 (the Kao Corp. make, nonionic surfactant)

The 0.05 weight section The 0.55 weight sections Potassium silicate water solution (26 % of the weight of SiO<sub>2</sub> content, 13 % of the weight of K<sub>2</sub>O content)

The 2.2 weight sections The 6.0 weight sections Potassium hydroxide The 1.5 weight sections The 3.1 weight sections Potassium sulfite The 0.9 weight sections 1% water solution of the penetrant remover \*\* sodium dehydroacetate before 0.8% water-solution development of the front [ 0.05% tap water solution development ] penetrant remover \*\* dialkyl sulfo sodium succinate of the penetrant remover \*\* ethylenediaminetetraacetic acid before 1.8 weight sections development [0096]

[Effect of the Invention] In an art including the processing which according to this invention washes the photosensitive lithography version with wash water, and removes this overcoat layer before development after image exposing the photosensitive lithography version which has a water-soluble overcoat on a sensitization layer Circulate through the wash water used for washing before development, and when using it repeatedly, according to invention concerning claim 1 According to invention which the problem a calcium carbonate carries out [ a problem ] deposition to piping which lets the inside of the tub which puts in the wash water which is used for washing before development, and which carries out a circulation reuse, and this wash water pass is solved, and relates to claim 2 The problem to which the washing processing speed by the rise of the resin concentration in the wash water which carries out a circulation reuse falls is solved, and according to invention concerning claim 3, the problem which mold generates in the wash water which carries out a circulation reuse is solved.

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[Translation done.]